REPORT DOCUMENTATION PAGE

DTIC FILE COPY

1a REPORT SECURITY CLASSIFICATION Unclassified	**1b RESTRICTIVE MARKINGS**

DTIC
ELECTE
JUL 27 1990
D

AD-A225 159

3 DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited
5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a NAME OF PERFORMING ORGANIZATION Diamond Materials, Inc.	**6b OFFICE SYMBOL** *(If applicable)*	**7a. NAME OF MONITORING ORGANIZATION** Office of Naval Research
6c. ADDRESS (City, State, and ZIP Code) ONE RAY AVENUE BURLINGTON, MASSACHUSETTS 01803		**7b. ADDRESS (City, State, and ZIP Code)** Code 1114 800 N. Quincy Street Arlington, VA 22217-5000
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	**8b. OFFICE SYMBOL** *(If applicable)*	**9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER**
8c. ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington, VA 22217-5000		**10. SOURCE OF FUNDING NUMBERS**

PROGRAM ELEMENT NO.	**PROJECT NO.**	**TASK NO.**	**WORK UNIT ACCESSION NO**
	4000047		sbi 01

11 TITLE (Include Security Classification)

Synthesis of Large Area, Monocrystalline TiC as a Substrate for Heteroepitaxial Growth of β-SiC

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13a. TYPE OF REPORT Final	**13b. TIME COVERED** FROM 89/9/7 TO 90/6/30	**14. DATE OF REPORT (Year, Month, Day)** 1990, JULY 23	**15. PAGE COUNT** 29 PAGES

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			**18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)**
FIELD	**GROUP**	**SUB-GROUP**	Beta silicon carbide, silicon, heteroepitaxy, titanium carbide.

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

The purpose of this program was to investigate an alternative method of synthesizing large area TiC monocrystals by a procedure involving multiple chemical vapor deposition (CVD) steps. The proposed method consisted of (a) heteroepitaxial growth of β-SiC on Si by CVD, (b) gettering of defects in the β-SiC, and (b) heteroepitaxial growth of TiC on β-SiC by CVD. Because of numerous technical difficulties, DMI's effort was limited to CVD of β-SiC on Si. DMI developed a process to etch Si and deposit β-SiC on Si at a constant temperature of 1300°C without cycling the temperature between etching step and CVD step. β-SiC was grown using methyltrichlorosilane (CH_3SiCl_3) without prior carburizing the Si surface. The microstructure of the deposited β-SiC film evolved from highly oriented cubic subgrains which coalesced into a smooth, continuous film.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	**21. ABSTRACT SECURITY CLASSIFICATION** UNCLASSIFIED
22a. NAME OF RESPONSIBLE INDIVIDUAL	**22b. TELEPHONE (Include Area Code)** | **22c. OFFICE SYMBOL**

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted.
All other editions are obsolete

FINAL REPORT

Synthesis of Large Area, Monocrystalline TiC as a Substrate
for Heteroepitaxial Growth of β-SiC

Time period:

September 7, 1989 to June 30, 1990

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Contract No. N00014-89-C-0208

Research Funded and Managed by:

Office of Naval Research

Approved for public release: Distribution Unlimited

FINAL REPORT

Synthesis of Large Area, Monocrystalline TiC as a Substrate
for Heteroepitaxial Growth of β-SiC

1.   INTRODUCTION

The purpose of this program was to investigate an alternative method of
synthesizing large area TiC single crystals. TiC monocrystals can serve as substrates
for the heteroepitaxial growth of semiconductor-grade β-SiC.

β-SiC semiconductor devices offer the promise of someday replacing vacuum
tubes as the source of microwaves for radar and communications. Because the cubic
("beta" or "3C") polytype of SiC is unstable at the sublimation temperature of SiC, the
only methods demonstrated to produce large, single crystals of β-SiC have been
heteroepitaxial growth by chemical vapor deposition (CVD). Monocrystalline Si, α-SiC,
and TiC are all viable substrates for the heteroepitaxial growth of monocrystalline β-
SiC. Of the three substrates, only TiC has been demonstrated to produce
monocrystalline β-SiC films free of stacking faults, misfit dislocations, inversion
domain boundaries, and double positioning boundaries. Additionally, TiC offers the
advantage of being a good electrical conductor, exhibiting excellent ohmic contact to n-
type β-SiC with low contact resistance; (J. D. Parsons, G. B. Kruval, and J. A. Vigil, in
Amorphous and Crystalline Silicon Carbide II, ed. by Rahman, Yang and Harris,
Springer-Verlag, New York, (1989) p. 171). Therefore, β-SiC single crystal films grown
on TiC substrates would be ideally suited for the fabrication of vertical FETs. Vertical
FETs, such as the permeable base transistor (PBT), have achieved high-power/high-
frequency operation when fabricated in Si and GaAs.

CVD of monocrystalline β-SiC films on TiC has been limited by the
unavailability of large area, TiC single crystals. TiC has materials properties which
make it difficult to grow as a large, monocrystalline boule by traditional crystal
growing methods such as the float zone process. The economic viability of β-SiC
semiconductors may depend on the production of large-area TiC single crystals.
Conventional TiC crystal growing methods (such as the float zone process) seem
unlikely to synthesize large diameter, (≥ 2 cm), monocrystalline boules of pure TiC free
of pores, pinholes, and subgrain boundaries.

For this SBIR Phase I program, Diamond Materials, Inc. (DMI) proposed a novel
procedure for the synthesis of large area TiC monocrystals. The proposed procedure
was the following sequence of steps: (1) heteroepitaxial growth of β-SiC on Si wafers by

chemical vapor deposition (CVD), (2) selective removal of the silicon wafers, (3) gettering of crystallographic defects in the β-SiC surface by chlorinated oxidation, and (4) heteroepitaxial growth of TiC on β-SiC by CVD. Deposition of β-SiC was performed using methyltrichlorosilane ("MTS," CH_3SiCl_3) as the source vapor for silicon and carbon.

2.   EXPERIMENTAL PROCEDURE AND RESULTS

Diamond Materials, Inc. performed as much as it could on the proposed statement-of-work. However, chronic technical problems and time constraints limited performance of the statement-of-work to experiments on the CVD of β-SiC on Si substrates.

2.1   De-bugging the β-SiC Reactor

DMI designed and built a CVD reactor to grow β-SiC during a previous SBIR contract funded by SDIO. It was a vertical flow, cold wall, low pressure CVD reactor. Substrates were suspended face down on a SiC-coated graphite faceplate, and heated by a graphite susceptor resting atop the substrate. The susceptor was heated by induction coils powered by a 450 kHz, 10 kW power supply. Substrate surface temperature was measured in-situ by an optical pyrometer. The chamber pressure could be controlled at 250 torr by a special throttle valve.

At the start of the program, DMI's β-SiC CVD reactor underwent extensive engineering modifications and additions, including: (a) a quick response gas handling system, (b) a completely redesigned "bell jar" assembly utilizing standard sized fused silica tubes, (c) a redesigned susceptor assembly, (d) an increase in the number of mass flow controllers (MFCs) to ten, and (e) a heating system which maintained the MTS bubbler, the MTS MFC and the MTS stainless steel tubing at a constant temperature of 50°C to mitigate condensation of MTS downstream from the bubbler. (The boiling point of MTS is 66°C).

Several days were spent determining the necessary sequence of pneumatic valve positions and MFC actuation in order to ensure the proper flow. The MTS valving was complicated since the special MTS bubbler (purchased from ATM, Inc.) was versatile, enabling direct flow of MTS impelled by MTS vapor pressure, or assisted flow of MTS using a H_2 carrier gas. After experimentation, it was decided to flow pure MTS through

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its MFC without any assistance from a carrier gas in order to maximize MTS flow accuracy and precision.

Minor problems were encountered and solved, such as replacement of defective MFC cables, cracked silica bell jars; and depletion of MTS supply. Since the β-SiC needed for this Phase I program did not have to be of "semiconductor grade" purity, DMI employed reagent-grade MTS which was 98% pure packed in Ar. Although the β-SiC films were undoubtedly doped with residual nitrogen, the reagent-grade MTS was available in the necessary quantities without the weeks of lead time needed for a vendor to perform MTS purification.

2.2   Approach to β-SiC Heteroepitaxy on Si

Based on conversations with experts, and by reading the literature, DMI felt that the optimal process for CVD of heteroepitaxial β-SiC on Si should be isothermal, or as close to isothermal as possible. The original procedure described by J. A. Powell and co-workers, (e.g., J. A. Powell, in Novel Refractory Semiconductors, edited by Emin, Aselage and Wood, Mat. Res. Soc. Symp. Proc. Vol. 97, (1987) p. 159), called for a two-step procedure where an initial thermal excursion is performed to etch the silicon in HCl/H_2, and a subsequent excursion is performed to first carburize and then deposit β-SiC from hydrocarbon + silane (SiH_4) mixtures. The reason for cooling to room temperature after the HCl etch was probably to ensure complete purging of residual HCl from the CVD reactor before starting nucleation and growth of β-SiC.

Methyltrichlorosilane, (CH_3SiCl_3), is a source gas which decomposes as:

$$CH_3SiCl_{3(v)} = SiC_{(s)} + 3HCl_{(v)}$$
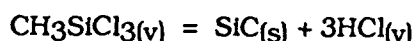
Hence, deposition of β-SiC from MTS includes a concurrent HCl etching phenomenon which helps prevent the co-deposition of elemental silicon, graphite and α-SiC. DMI decided to deposit β-SiC immediately following the HCl etch step without cooling the substrate to room temperature.

The use of MTS made it unnecessary to carburize the silicon surface in order to nucleate a monocrystalline β-SiC layer. Carburization of the silicon surface is performed by exposing Si to a hydrocarbon + H_2 mixture at temperatures ≥ 1300°C; an ultrathin, heteroepitaxial β-SiC layer is formed. The carburization step was shown to generate defects in heteroepitaxial β-SiC in research performed by Molnar and Shirey of the Naval Research Laboratory, (poster F8.7 presented at the Fall 1989 Materials

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Research Society meeting, "SEM Observation of Growth and Defect Formation on Heteroepitaxially Grown SiC on (100) Silicon.") Molnar and Shirey noted that a localized excess of reactive carbon at the silicon surface (i.e., during carburization) prompts outdiffusion of silicon from the near-surface region, creating microscopic "potholes" beneath the β-SiC film which exacerbate β-SiC film stress. Flowing a hydrocarbon over a silicon surface $\geq$ 1300°C *without* also flowing a silicon source (e.g., silane) invites excessive outdiffusion of silicon from the substrate.

As demonstrated by Nishino and Saraie, ("Epitaxial Growth of 3C-SiC on a Si Substrate Using Methyltrichlorosilane," in Amorphous and Crystalline Silicon Carbide, ed. by Harris and Yang, Springer-Verlag (1989) p. 45), carburization with a hydrocarbon is unnecessary to nucleate β-SiC when using MTS. Nishino and Saraie directly nucleated and grew heteroepitaxial β-SiC using 1 sccm of MTS plus 1 SLM of H_2 at 1300°C, (i.e., 0.1% MTS/H_2). Prior to MTS flow, they performed a separate temperature excursion for HCl/H_2 etching, which DMI believed was unnecessary.

DMI's goal was to develop a CVD procedure for β-SiC growth on Si composed of: (1) pump down to ultimate vacuum, (2) backfill with hydrogen to 250 torr and maintain that pressure for all subsequent steps, (3) heat up in H_2 to a fixed temperature, (4) add HCl/H_2 to etch the silicon surface, (5) immediately switch off the HCl and add MTS/H_2 to nucleate and grow β-SiC, (6) turn off the MTS/H_2 and cool to room temperature in argon.

2.3 Hydrogen Etching Experiments

At the beginning of this program, DMI believed that the purpose of the HCl/H_2 etch step was simply to remove native oxide (SiO$_2$) from the Si surface. Hence, an initial goal was to determine a heat up and etch sequence which would produce a flat, pinhole free silicon surface which would be free of native oxide immediately before commencing MTS flow.

Heat up experiments were performed in H_2. It was concluded that heat up in H_2 is preferable to heat up in Ar because of the significantly higher thermal conductivity of H_2. Switching from Ar to H_2 would make it difficult to maintain substrate temperature continuity. Since the substrate is inductively heated, a sudden switch from Ar to H_2 would cause the substrate temperature to plummet faster that the rf power supply could respond.

All experiments performed in the β-SiC reactor shared a number of similarities. The total pressure was fixed at 250 torr, maintained by a special high pressure throttle

valve working in concert with a capacitance manometer. The wafers were cleaned according to the standard RCA procedure before being inserted into the reactor. It was observed that pure H_2 had the ability to etch the silicon surface. A series of runs were performed to determine the temperature to which silicon would be heated without H_2 etching. This temperature was determined to be 1000°C.

2.4 HCl/H_2 Etching Experiments

After H_2 etching was investigated, DMI began performing HCl/H_2 etching experiments. Again, DMI believed that the reason why all published recipes for β-SiC heteroepitaxy included a preliminary etch was to remove native oxide. HCl/H_2 etching experiments were performed at temperatures between 1000 and 1300°C and at concentrations between 1% and 5% HCl diluted in H_2. It was observed that pitting of the silicon surface was almost always observed when flowing HCl except when the temperature was below 900°C.

After close microscopic examination of the etch pits, and re-examination of the published HCl etch recipes, it became clear that DMI had *misinterpreted* the true reason for the HCl etch step. All of DMI's H_2 and HCl etch experiments were simply decorating crystalline defects present in the surface of silicon wafers. The chem-mechanical methods used to polish all semiconductor-grade silicon leaves the near-surface region of the silicon crystal riddled with stacking faults and other point and line defects. Defect gettering from the silicon surface is typically accomplished by HCl/O_2 oxidation. DMI's mild HCl etch experiments were simply identifying the presence of crystalline defects near the wafer surface. DMI realized that the *real* motivation for the HCl etch prior to β-SiC growth is to etch away *several microns* of silicon to expose fresh, defect-free silicon. Because the contribution of the hydrogen etch to the total HCl/H_2 etch was minor, the pure H_2 etch portion of the procedure was eliminated.

DMI obtained a desirable result by increasing the aggressiveness of the HCl etch procedure. In run 44, 5 sccm of HCl plus 95 sccm of H_2 were run for 5 minutes at 1300°C, with cool down in argon. The result was the formation of a layer of silicon which had almost completely detached from the silicon surface. The silicon layer was several microns thick, and was bowed upward, still attached to the substrate at the center. In run 46, the process conditions of run 44 (5% HCl/H_2 at 1300°C) were repeated for a longer time, 10 minutes, and resulted in complete removal of the defective layer of silicon. Figure 1 is a SEM micrograph of the flat bottom hole cut into the silicon wafer
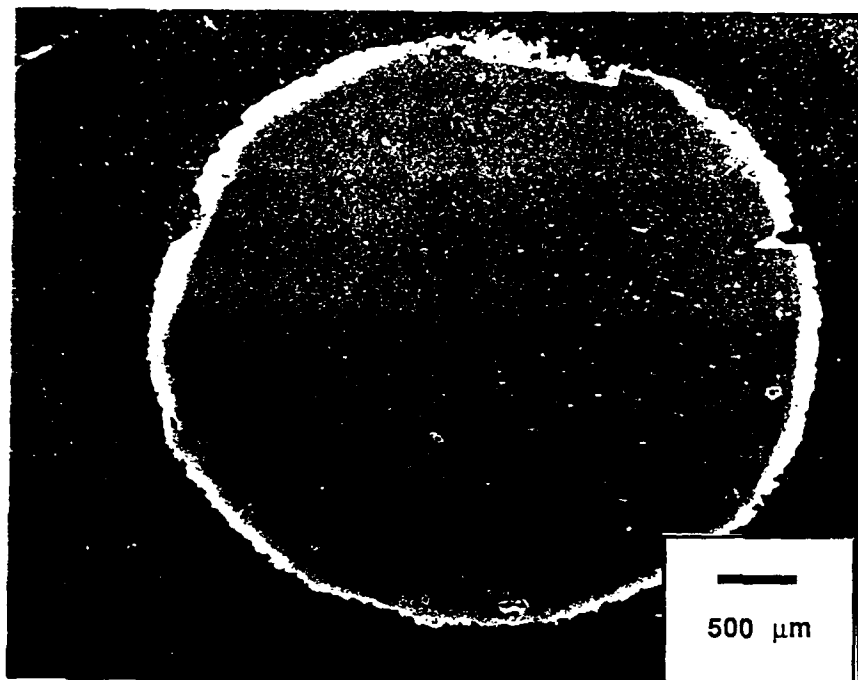
FIGURE 1. Run 46. SEM micrograph of flat-bottom crater in silicon created by 10 minutes of 5% HCl/H2 etching at 1300°C.

500 μm

during run 46. The hole is ≈5 μm deep and has a rather smooth texture at its bottom. It is apparent that the HCl had to remove the outer 5 μm of silicon to reach a silicon region which etches at a uniform rate. Uniform etching over the area of the surface indicates a silicon region relatively free of crystallographic defects.

The etch procedure developed in run 46 was then instituted for all subsequent MTS runs. An etch temperature of 1300°C was desirable since CVD of of heteroepitaxial β-SiC should occur at a similar temperature.

2.5 β-SiC Growth Experiments

The initial β-SiC growth experiments were performed using ordinary silicon wafers oriented {100}. These experiments are summarized in Table 1. CVD of SiC using MTS immediately followed the 5% HCl/H_2 etch procedure defined by run 46.

Table 1: β-SiC Growth Experiments on {100} Si.

	Flow (sccm)			Duration	Temp.
Run	Hydrogen	MTS	% MTS	(min.)	(°C)
49	200	1	0.50	5	1300
52	300	1	0.33	5	1300
53	250	1	0.40	5	1300
59	300	3	1.0	5	1300
60	250	4.75	1.9	5	1300
63	250	4.75	1.9	5	1300-1400

SEM micrographs of samples 49 to 63 appear as Figures 2 - 8. Comparing the figures, it is apparent that the thickness of the films is proportional to the MTS percentage. The figures also indicate the evolution of β-SiC film microstructure. Figure 7B shows the edge view of a film. The β-SiC films grow in two stages. The initial stage is island growth of oriented β-SiC crystals. When seen in plan view, as in Figure 3B, these early crystals are oriented cubically, with 90° angles clearly seen in Figure 3B.

During run 63 the belljar viewport, used by the optical pyrometer to measure Si surface temperature, was occluded. Since optical pyrometer measurements automatically determines the power output from the rf power supply, rf output was boosted to compensate for a perceived loss of substrate temperature. The boosted rf
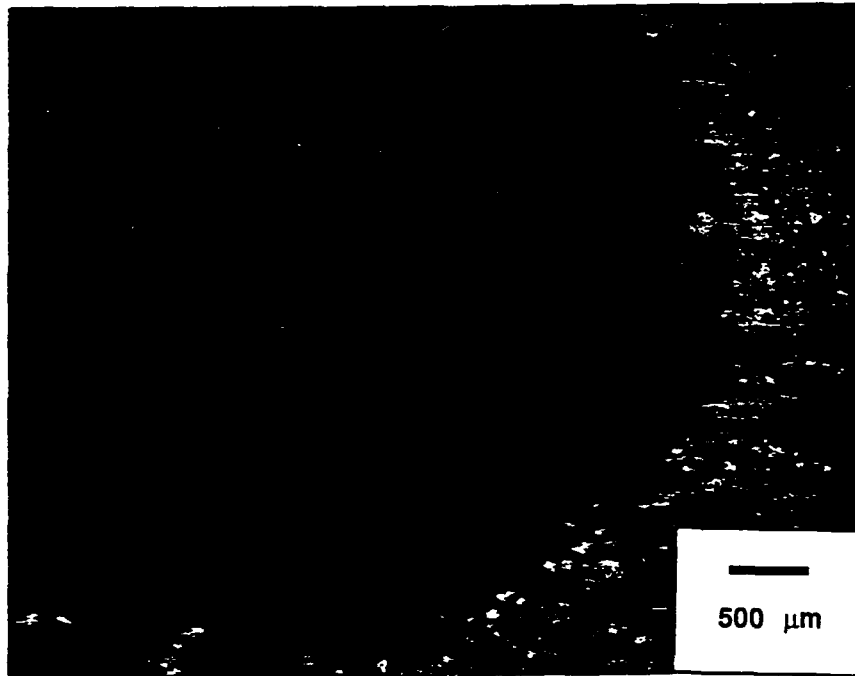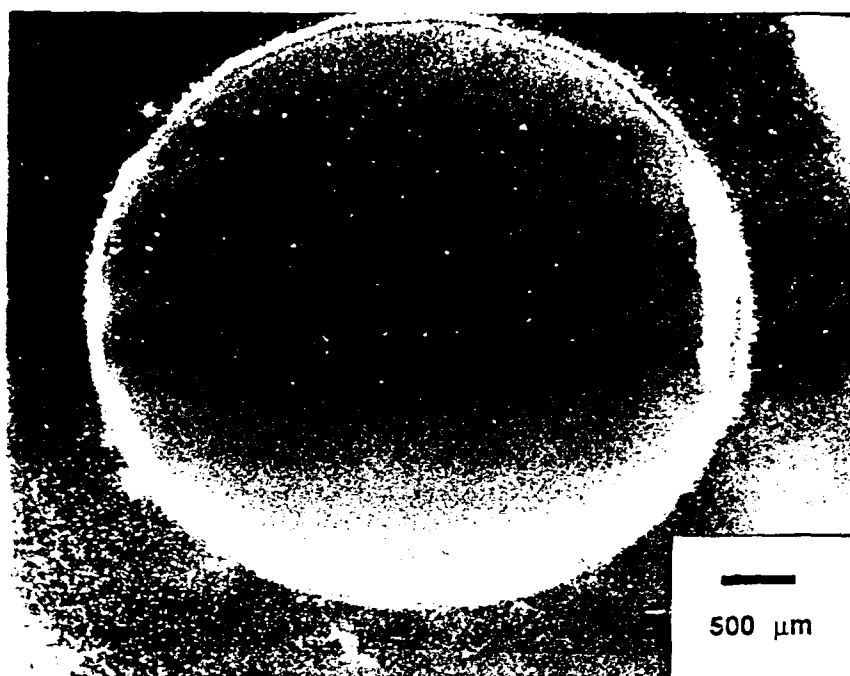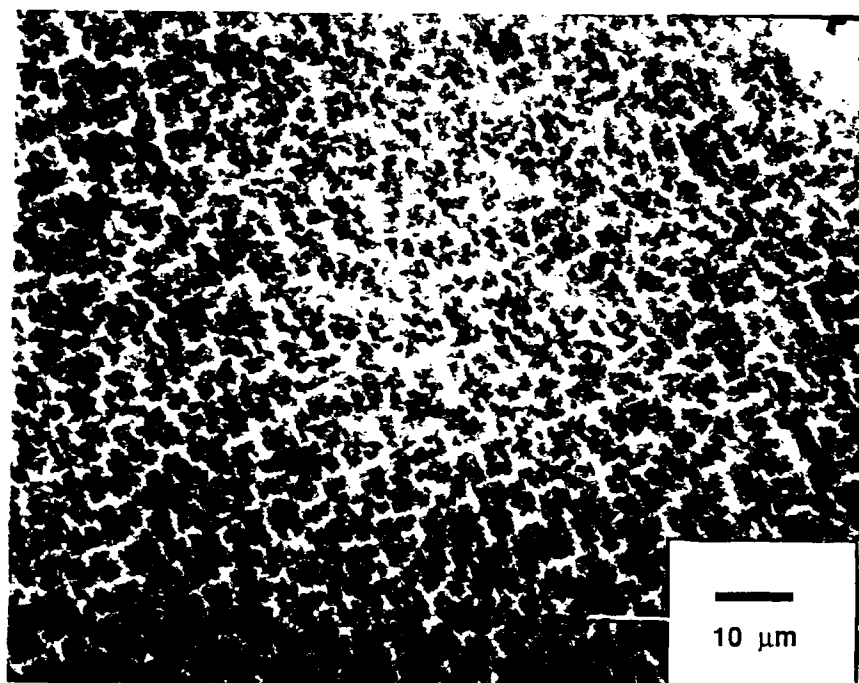
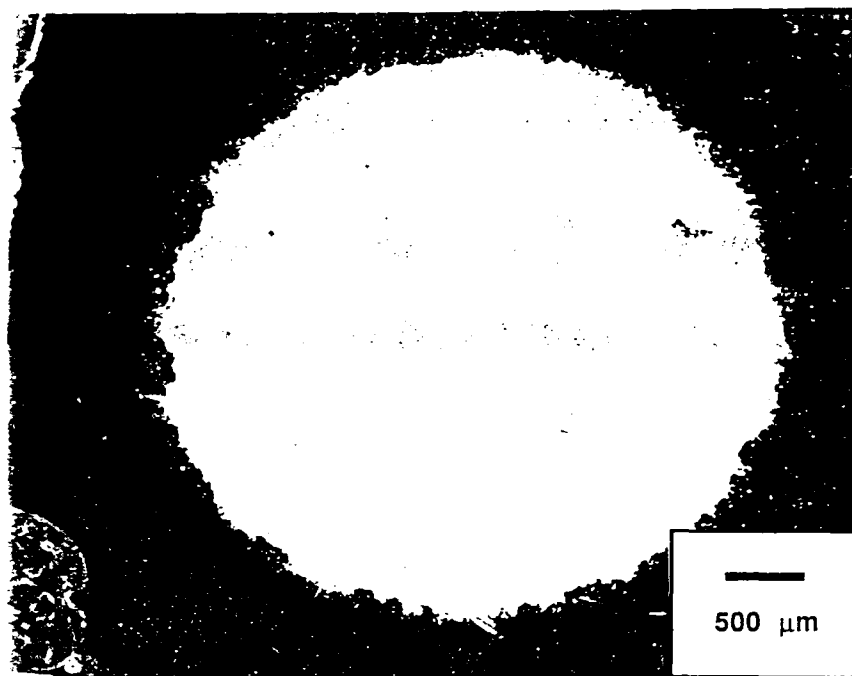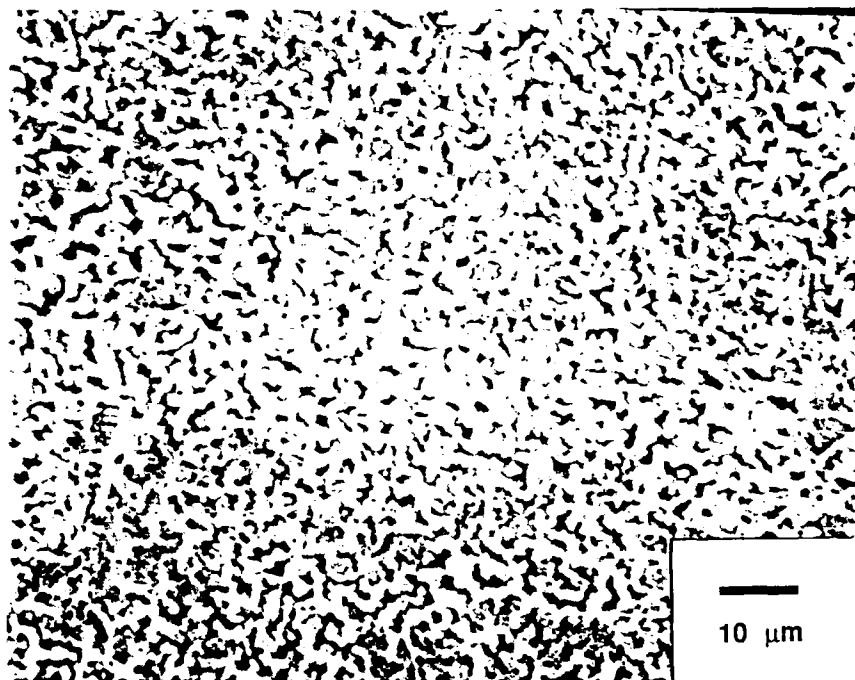FIGURE 2. Run 49. SEM micrograph of film grown from 0.50% MTS/H2 at 1300°C.

A

B

FIGURE 3. Run 52. SEM micrographs of film grown from 0.33% MTS/H2 at 1300°C.
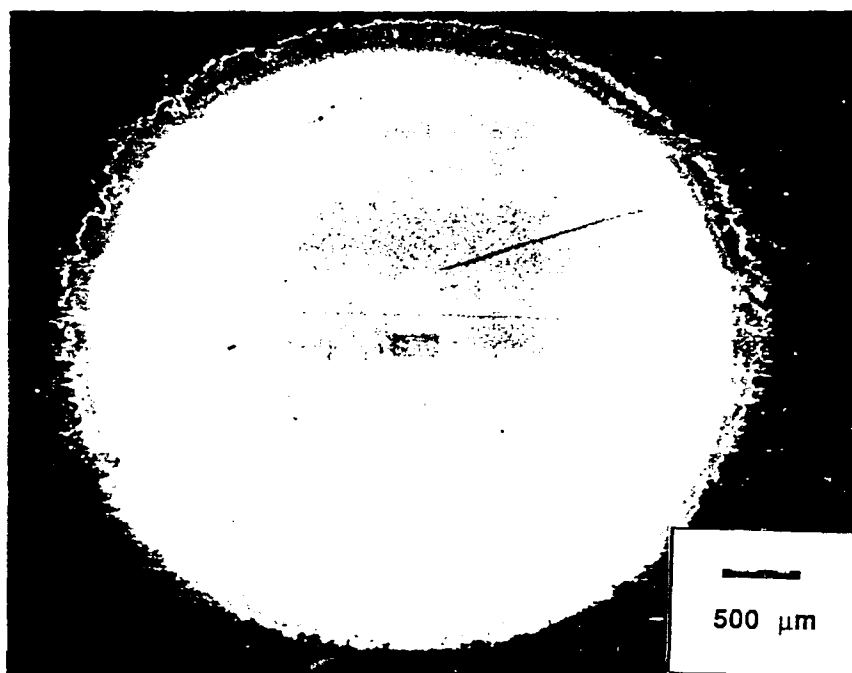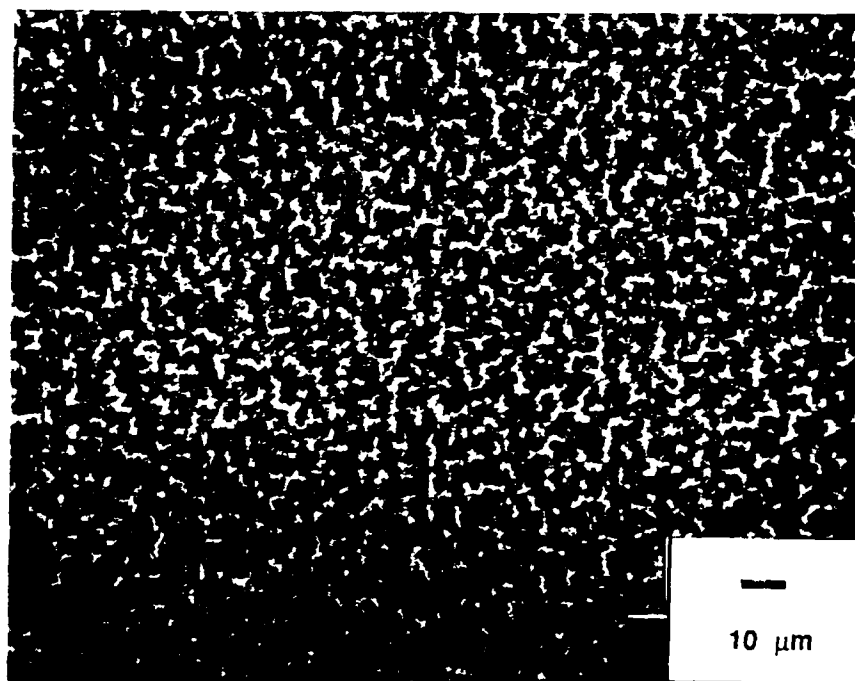
9

A

B

FIGURE 4. Run 53. SEM micrographs of film grown from 0.40%
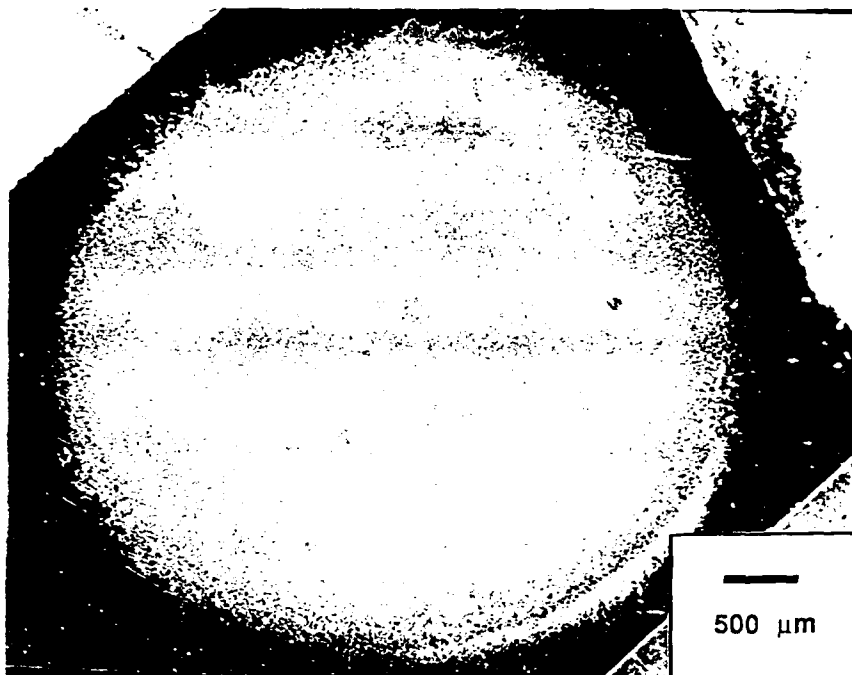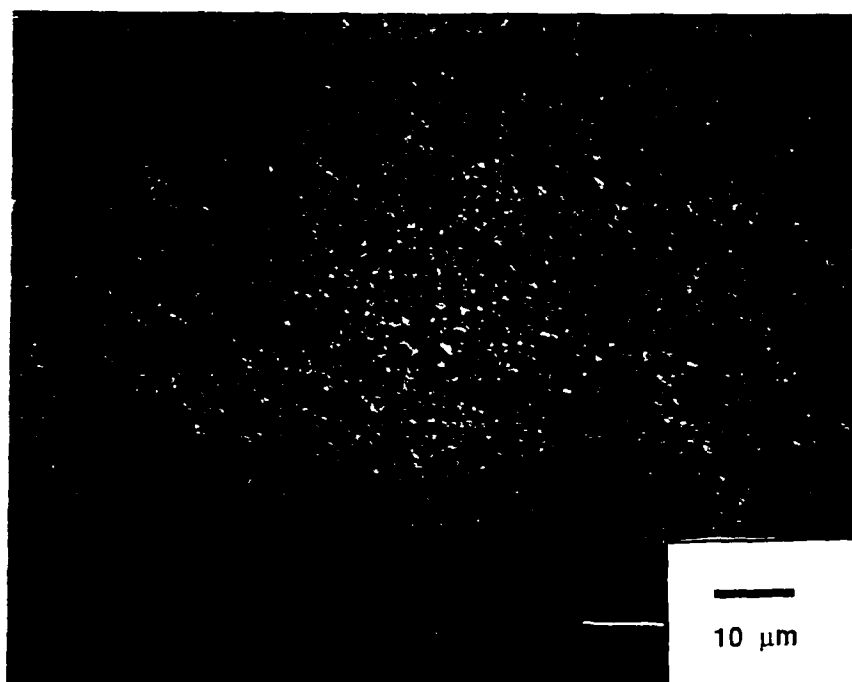MTS/H2 at 1300°C.

10

A

B

FIGURE 5. Run 59. SEM micrographs of film grown from 1.0% MTS/H2 at 1300°C.
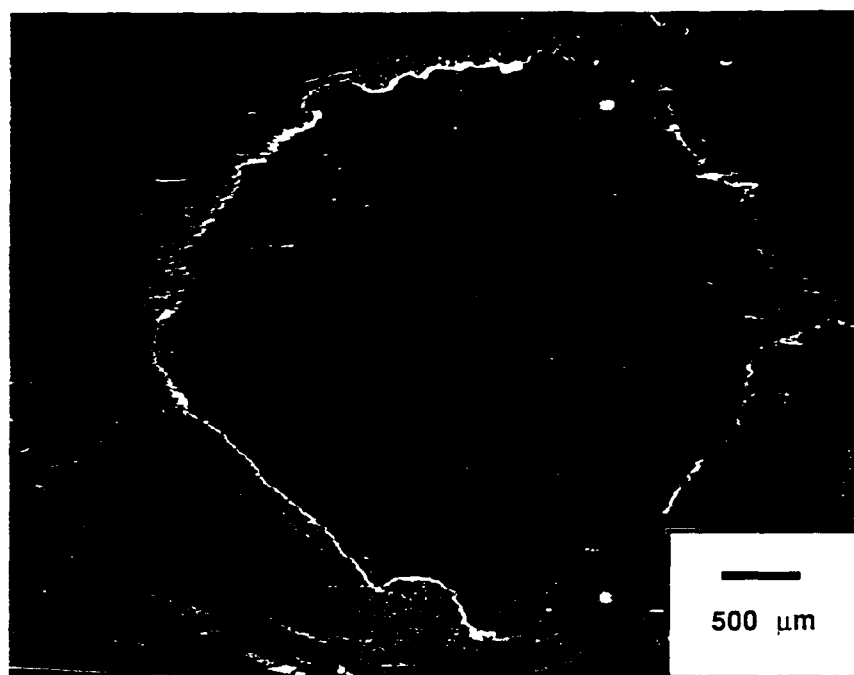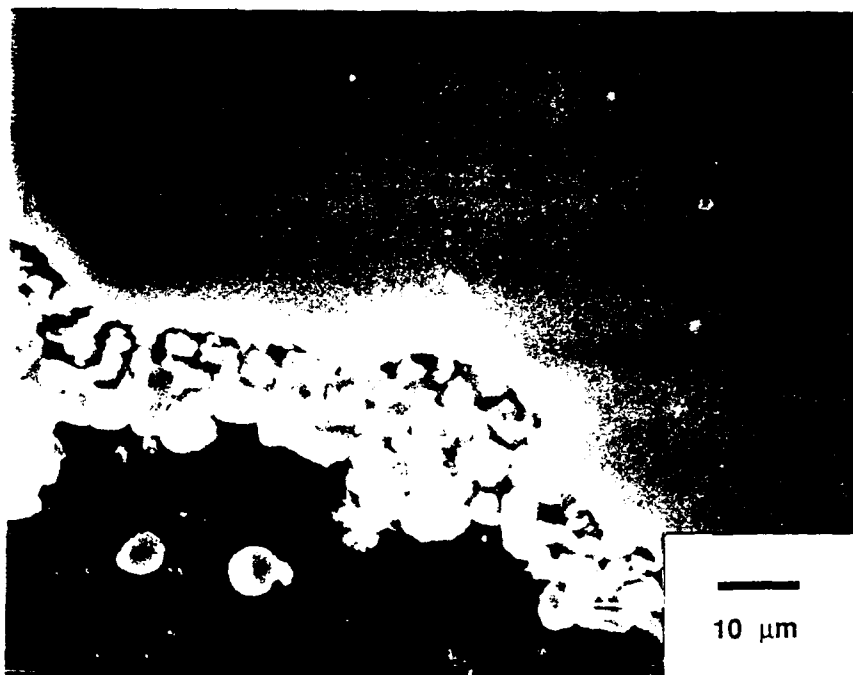
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A

B

FIGURE 6. Run 60. SEM micrographs of film grown from 1.9%
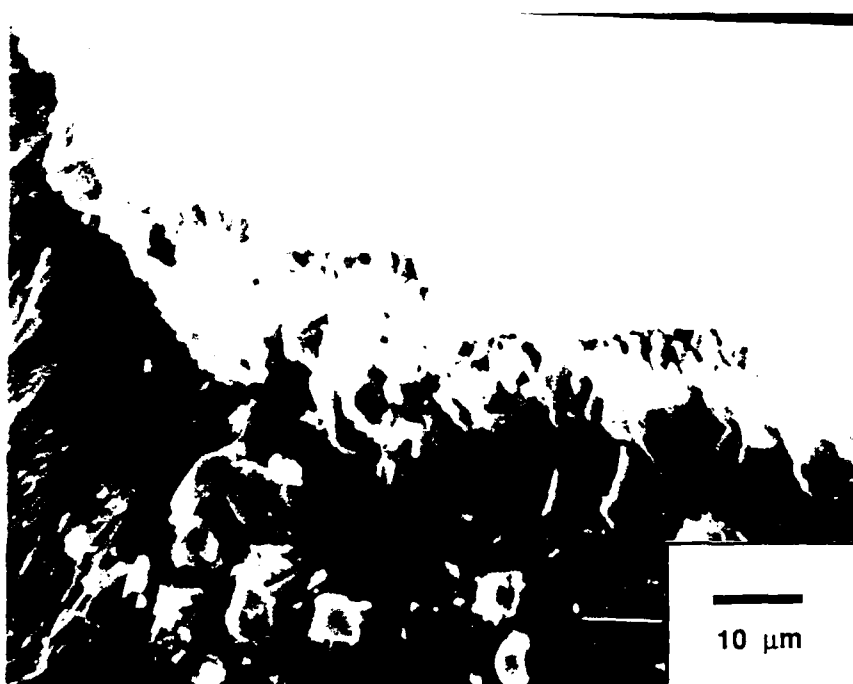MTS/H2 at 1300°C.

A

B

FIGURE 7. Run 63. Lower magnification SEM micrographs of film
grown from 1.9% MTS/H2 at 1300 - 1400°C.

13

A

B

FIGURE 8. Run 63. Higher magnification SEM micrographs of film
grown from 1.9% MTS/H2 at 1300 - 1400°C.

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power increased the substrate temperature to near the melting point of silicon (1410°C); after removal from the reactor, the perimeter of the silicon substrate was found to be partially melted.

There is evidence that run 63 may have been DMI's first heteroepitaxial β-SiC film on silicon. The film was optically transparent, with a very smooth and flat texture. The film had a slight greenish color under the optical microscope. Figures 7 and 8 indicate that the film was run long enough for the numerous subgrains to coalesce into a continuous film. The numerous subgrains had a thickness of 4-6 μm; the continuous smooth film atop the subgrains had a thickness under 1 μm. Under careful inspection of Figures 7B and 8B, *orange peel* surface texture is discernable. This microstructure reflects the transition of the SiC film from the etched surface at the bottom of the silicon crater to the smoother, orange peel surface at the top of the film.

Raman spectroscopy was used for qualitative analysis of the CVD deposited films. As illustrated in Figure 9, Raman spectroscopy can distinguish α-SiC from β-SiC. The Raman spectrum of film 63 was weak in intensity, as presented in Figure 10. The spectrum of film 63 indicates the presence of both α-SiC and β-SiC. A TO mode of α-SiC is observed at 786 cm^{-1} and a TO mode of β-SiC is at 798 cm^{-1}. Despite total thickness of the film being 5 - 7 μm, the weak Raman response is puzzling. The film may contain a high concentrations of crystallographic defects which reduce Raman intensity. The multiple subgrains seen in Figure 8B support this defective crystal theory.

After run #63, all SiC films were grown on silicon wafers cut and polished off axis. The wafers, purchased from Virginia Semiconductor, were cut and polished 0.5° ±0.25° off the (100) surface as rotated about the <110> axis. The silicon wafers were 10 - 12 mils (250 - 300 μm) thick. According to J. A. Powell, such off-axis Si substrates prevent the formation of inversion domain boundaries in heteroepitaxial β-SiC films grown on Si; (J. A. Powell and L. G. Matus, in Amorphous and Crystalline Silicon Carbide II, ed. by Rahman, Yang and Harris, Springer-Verlag, New York, (1989) p. 14). Several of the 2" diameter wafers were cut into smaller squares, 1 cm^2, and then cleaned according to the RCA procedure.

After the belljar and susceptor assembly was taken apart and cleaned, growth runs resumed using the off axis silicon. It was observed that the thin Si wafers tended to fuse to the graphite susceptor and the graphite faceplate. Therefore, a separate MTS CVD run was performed to coat the graphite faceplate and susceptor with SiC. Unfortunately, the alumina collar fractured, due to thermal fatigue during temperature cycling. This collar connected the graphite + sample + faceplate sandwich to the
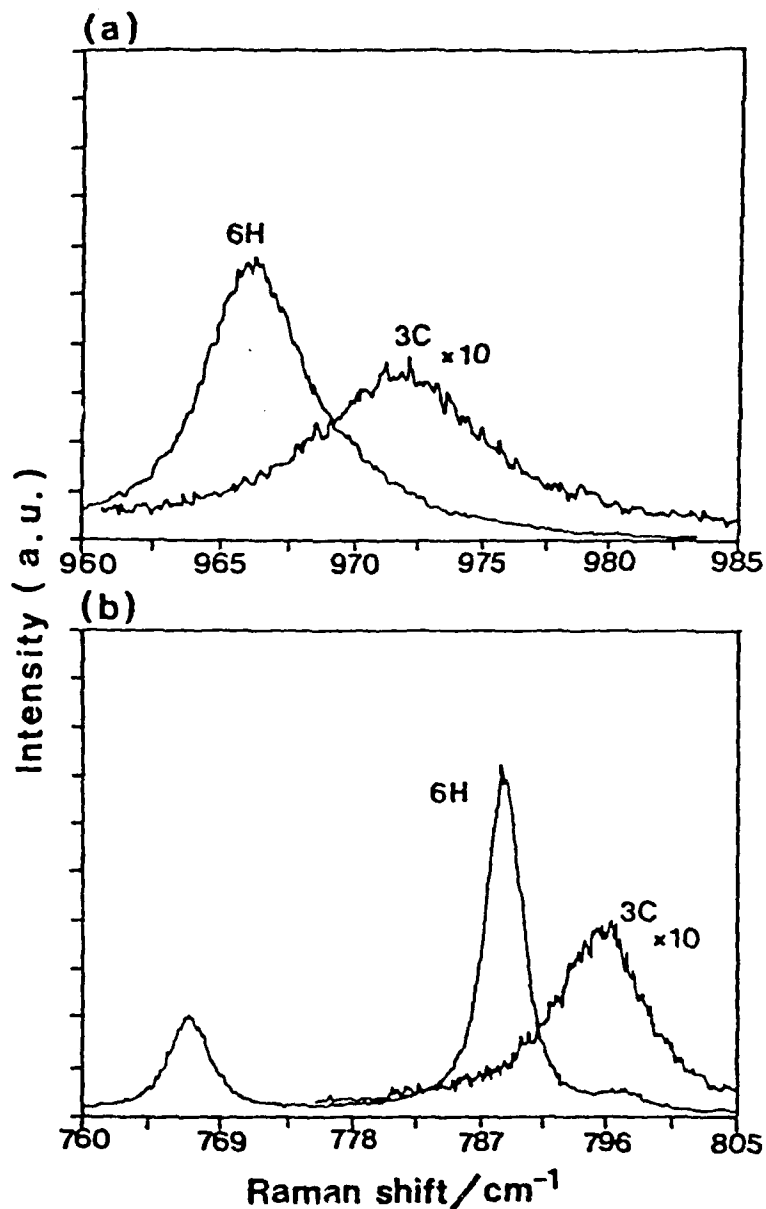
FIGURE 9 RAMAN SPECTRA OF 6H SiC AND 3C -SiC (ß-SiC). Spectrum (a) covers the region from 960 to 985 cm^{-1}, while (b) covers the region from 760 to 805 cm^{-1}. (Reproduced from H. Okumura, E. Sakuma, J. H. Lee, H. Mukaida, S. Misawa, K. Endo and S. Yoshida, "Raman Scattering of SiC: Application to the Identification of Heteroepitaxy of SiC Polytypes," *J. Appl. Phys,* 61 [3] 1134 (1987)).
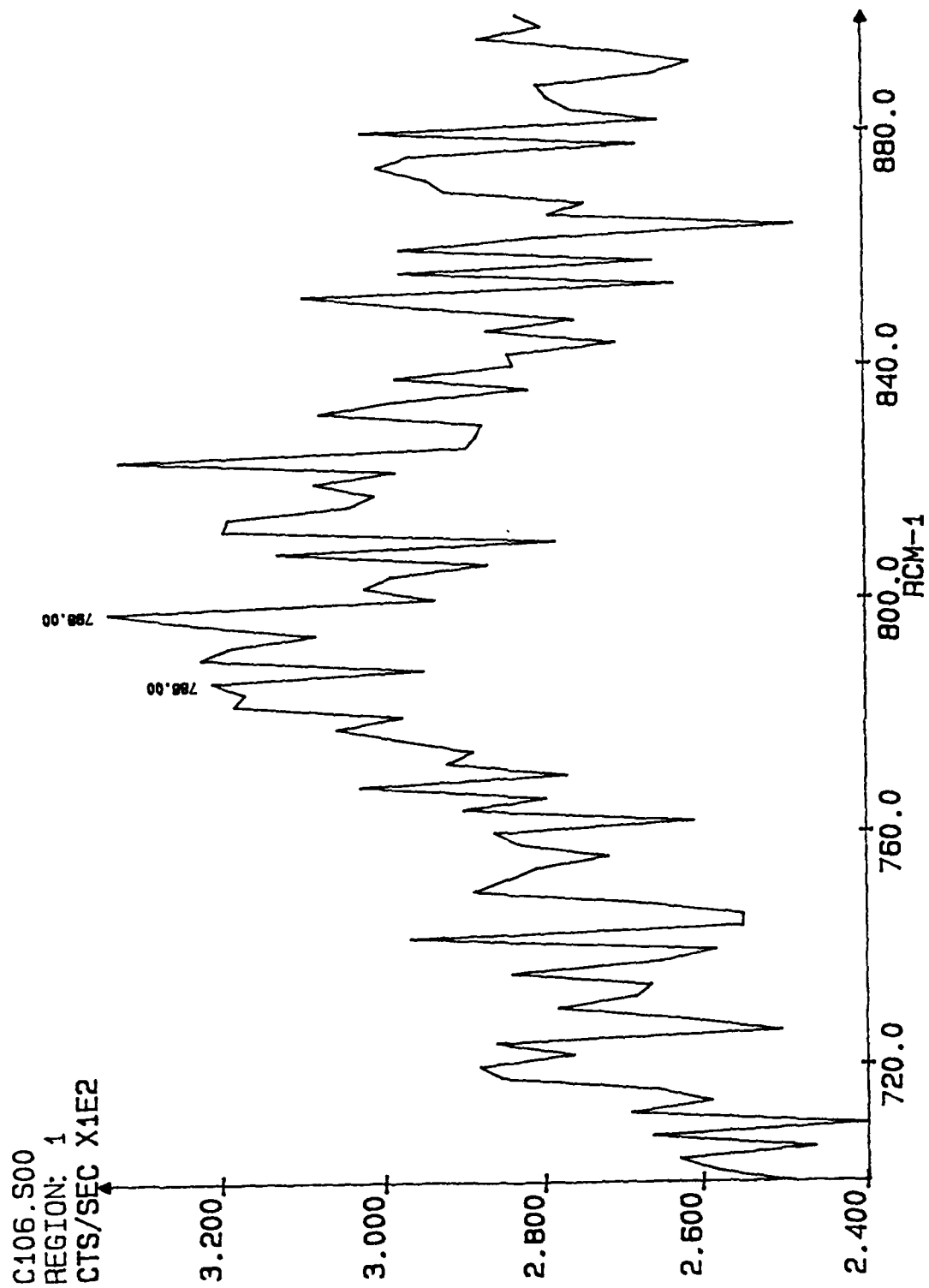
FIGURE 10 Raman spectrum of film grown by run 63. The TO mode of alpha silicon carbide is present at 786 cm-1 and the TO mode of beta silicon carbide is present at 798 cm-1.

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alumina shaft descending from the Ferrofluidics feedthrough atop the belljar. This small alumina collar was replaced by a larger alumina collar designed for 2" diameter silicon wafers. A 2" diameter graphite faceplate and susceptor were then tested with a full, 2" Si wafer. However, it was discovered that the susceptor assembly could not heat the Si substrate to a uniform temperature of 1300°C; the edges of the silicon was heated near the melting point of Si while the center was only 1070°C. The severe temperature gradient resulted from selective coupling of the rf power to the perimeter of the graphite susceptor. After performing only two runs with the 2" diameter susceptor assembly, the large alumina collar then fractured. Therefore, all remaining experiments used a spare, small alumina collar designed for 1 cm diameter substrates.

The SiC CVD growth experiments on off-axis silicon are summarized in Table 2.

Table 2: β-SiC Growth Experiments on 0.5° off (100) Si.

| Run | Flow (sccm) | | % MTS | Duration (min.) | Temp. (°C) |
	Hydrogen	MTS			
64	250	4.75	1.9	5	1325
65	250	4.75	1.9	10	1300
70	200	4.75	2.3	10	1300
73	250	4.0	1.6	10	1300
74	200	4.75	2.3	10	1300
75	250	4.75	1.9	10	1300
76	250	4.75	1.9	10	1300
78	250	4.0	1.6	10	1300
79	250	2.0	0.79	15	1300
80	250	1.0	0.40	20	1300
81	250	2.0	0.79	15	1300
82	250	2.0	0.79	15	1300-1230
83	250	2.0	0.79	15	1300
84*	250	4.0	1.6	10	1300
85*	250	4.0	1.6	15	1300
86*	250	4.0	1.6	10	1300
87*	250	4.0	1.6	15	1300

* Faceplate + substrate + susceptor sandwich suspended on graphite fibers.

Experiments not listed in Table 2 (e.g., run 66) were experiments which were aborted due to some equipment difficultly in mid-run. Common problems encountered during a run included uncontrolled attenuation of MTS flow, loss of temperature control due to occlusion of the optical pyrometer window, or fracture of the alumina collar as discussed previously. The corrosive nature of MTS, plus its boiling point of 66°C, made its use in an MFC, (rated for 10 sccm maximum flow), problematic since MTS tended to clog the capillary tube used to measure flow. The capillary tube was probably clogged with condensed MTS liquid, corrosion product, or with Si or SiC particles. Based on our experience, it is believed that the best flow controller for MTS should use large bore tubing and measure flow by a method other than capillary tubes, e.g., by a diaphragm manometer.

Figure 11 presents SEM micrographs of run 65. The MTS/H$_2$ mixture was flowed 10 minutes in experiment 65, but the other deposition conditions were the same as in run 63. Unfortunately, a smooth film was not obtained, and the Raman spectrum of sample 65 was similar to that of run 63, Figure 10.

Films grown from runs 65-78 shared a rough surface morphology. To increase surface smoothness (and promote heteroepitaxial growth of β-SiC), the growth rate was slowed by reducing the percentage of MTS diluted in hydrogen. Figure 12 contains SEM micrographs of run 79, performed using 0.8% MTS at 1300°C. The microstructure is similar to the oriented subgrains observed in run 59 (Figure 5). However, run 79 had the highest β-SiC purity of any film produced during this program, as evidenced by its Raman spectrum shown in Figure 13.

Experiment 81 was an attempt to replicate run 79. Occlusion of the optical pyrometer window caused the temperature to fluctuate between 1275 and ≈1330°C during film deposition. SEM micrographs of run 81 appear in Figure 14 and its Raman spectrum appears in Figure 15. The surface of film 81 appears to contain small fibers. The Raman spectrum indicates a two phase mixture of α-SiC and β-SiC, hence the fibers seen in Figure 14B are probably α-SiC.

During experiment 83, the last alumina collar fractured. Since the alumina parts were custom machined and required a couple months delivery, subsequent growths run using the spinning platen assembly were impossible. To continue work, runs 84 - 87 were performed by suspending the faceplate + sample + susceptor sandwich from three carbon fiber bundles. This new assembly enabled achievement of substrate temperatures of 1300°C, but the film properties were not reproducible. By run 86, a severe leak was discovered in the belljar, which was found to be due to a crack in the inner fused silica tube, the vacuum barrier. In run 87, the crack had grown large enough
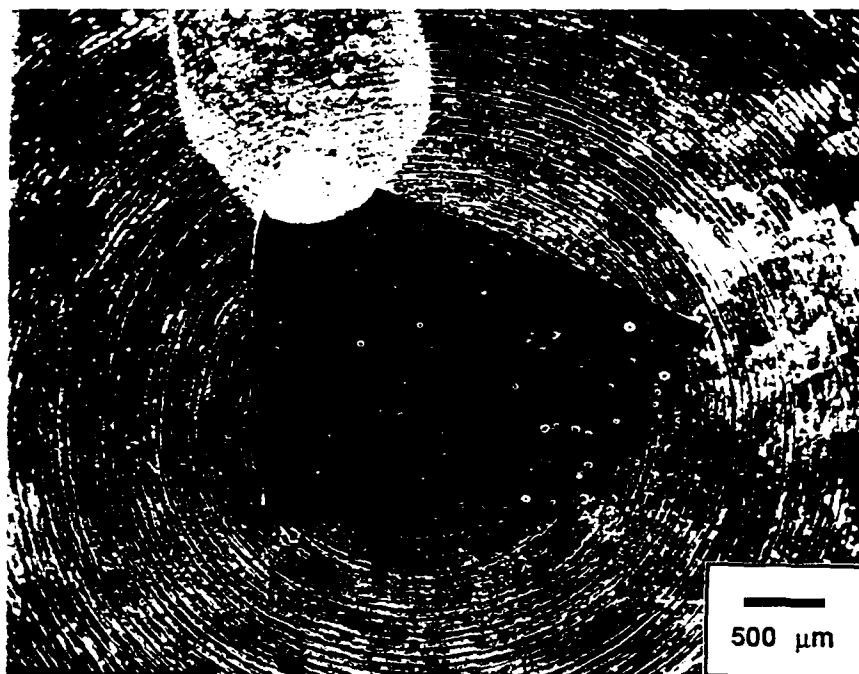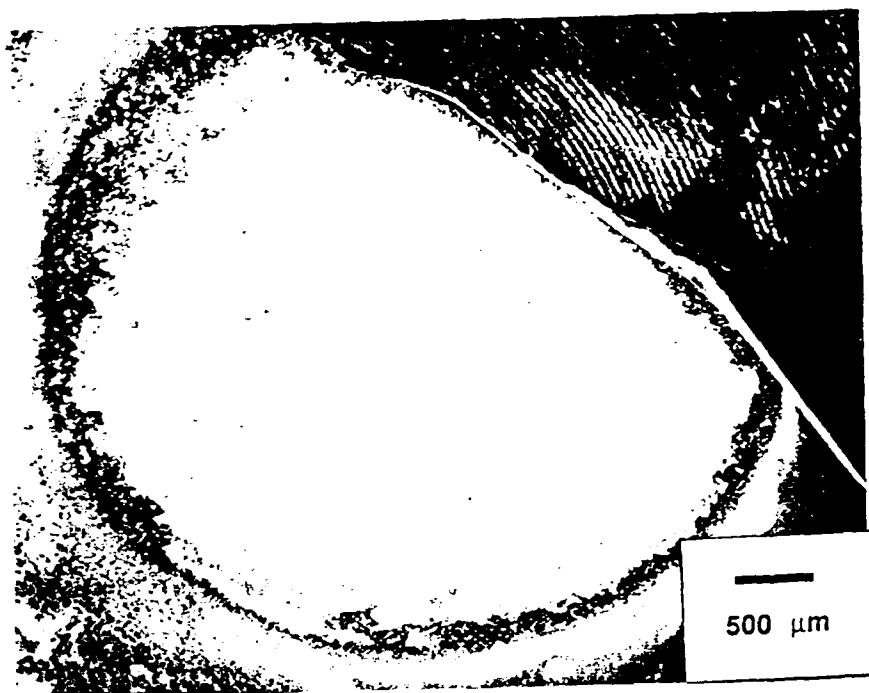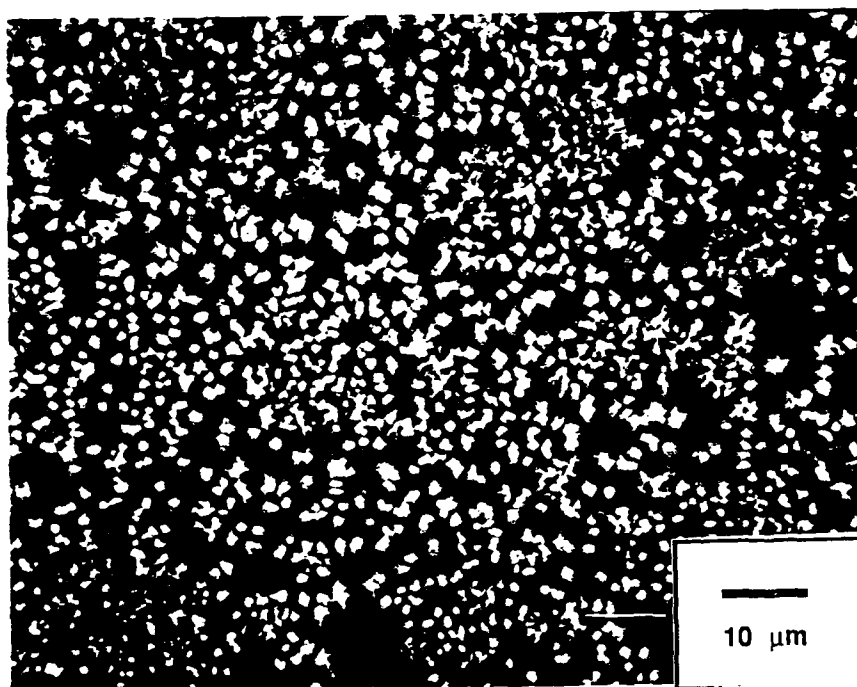
A
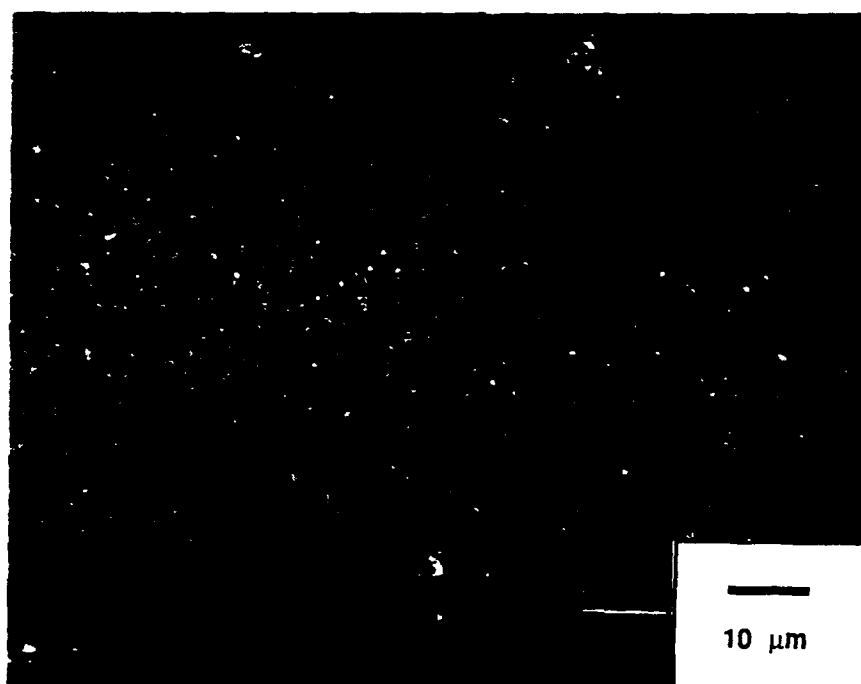
B

FIGURE 11   Run 65.   SEM micrographs of film grown from 1.4% MTS/H2 at 1300°C.

A

B

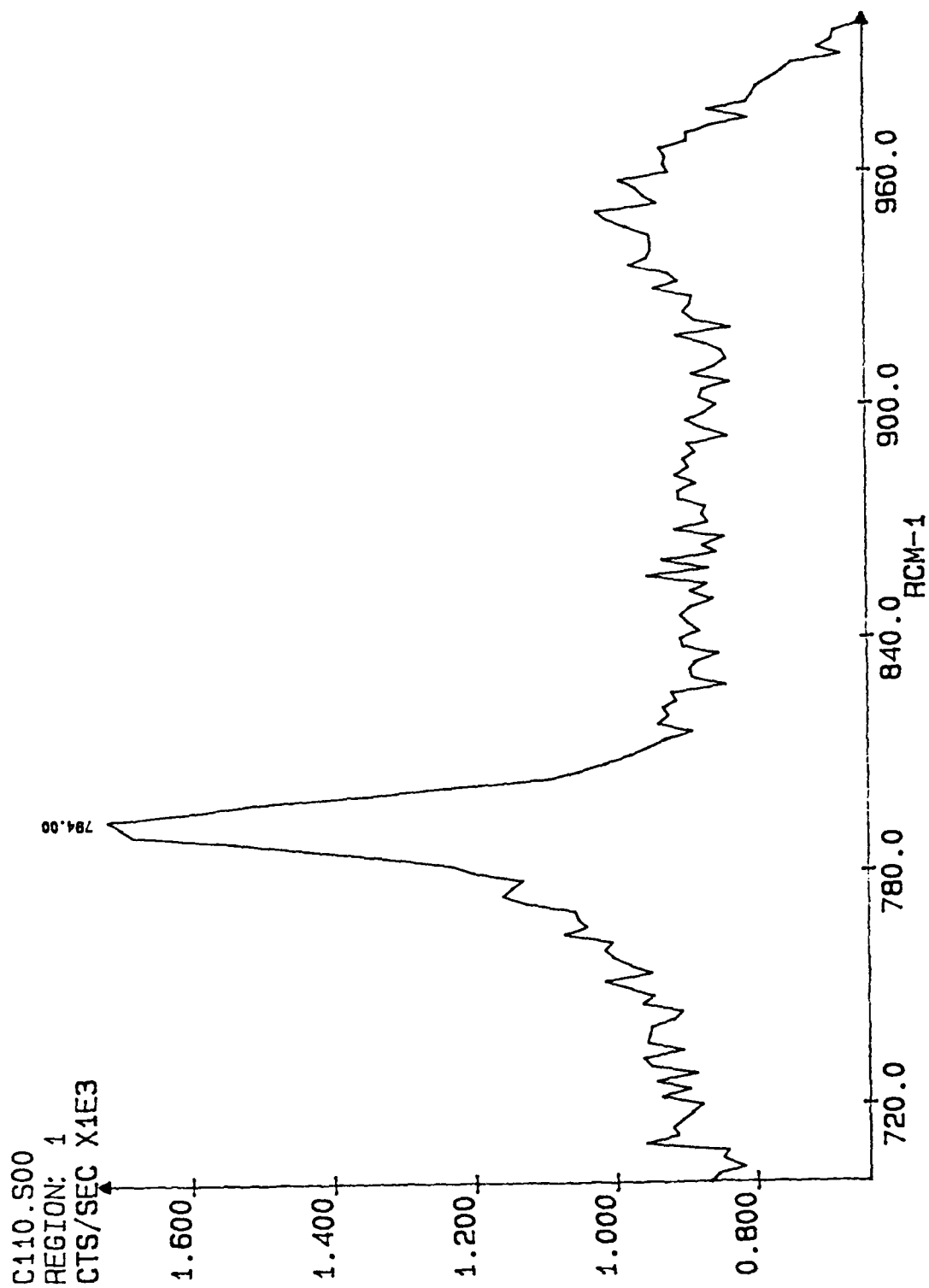FIGURE 12 Run 79. SEM micrographs of film grown from 0.8% MTS/H2 at 1300°C.
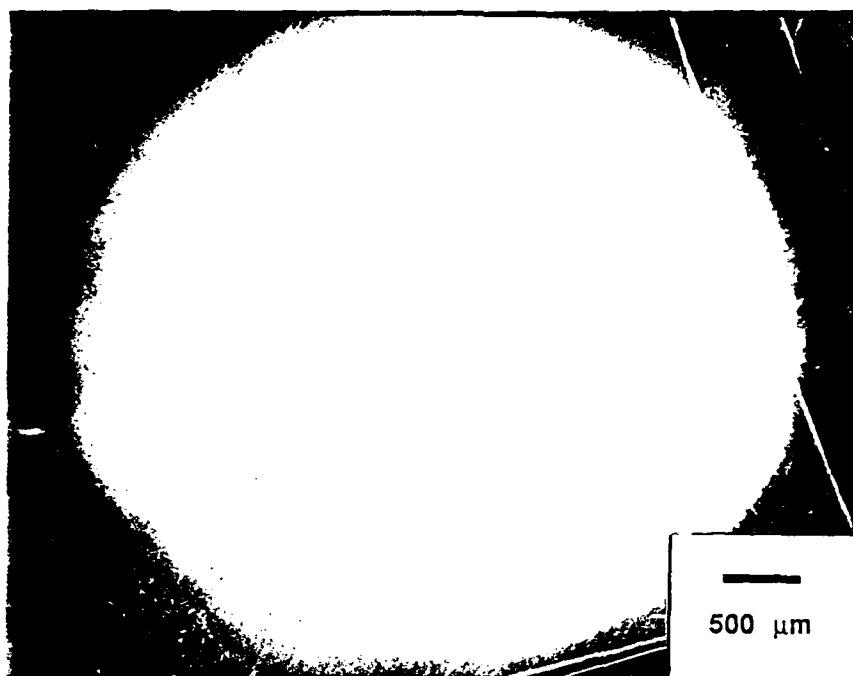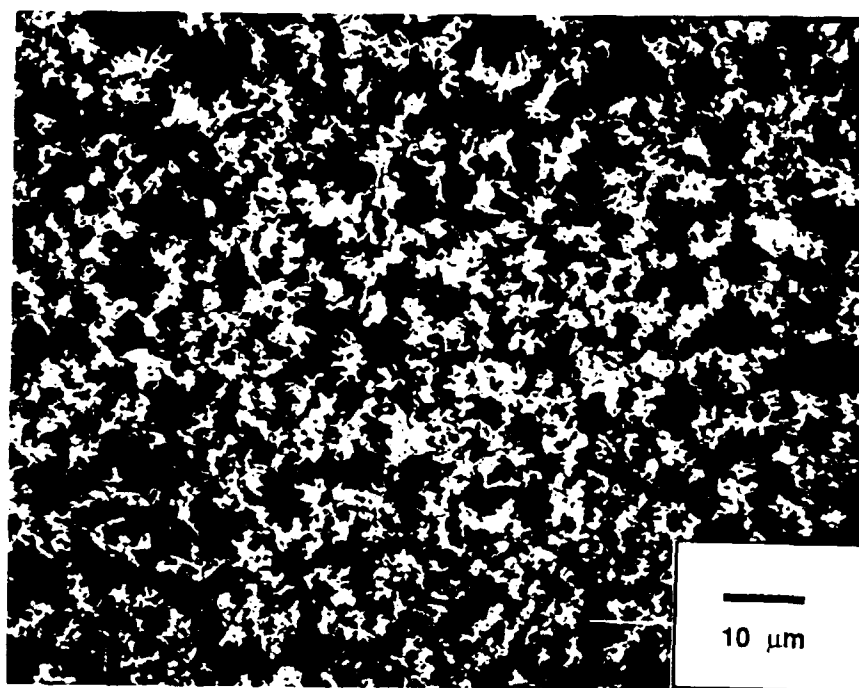
FIGURE 13 RAMAN SPECTRUM OF SAMPLE #79. ß-SiC peak is present at 794 cm^{-1}.

A

B

FIGURE 14 Run 81. SEM micrographs of film grown from 0.8% MTS/H2 at ≈1350°C.
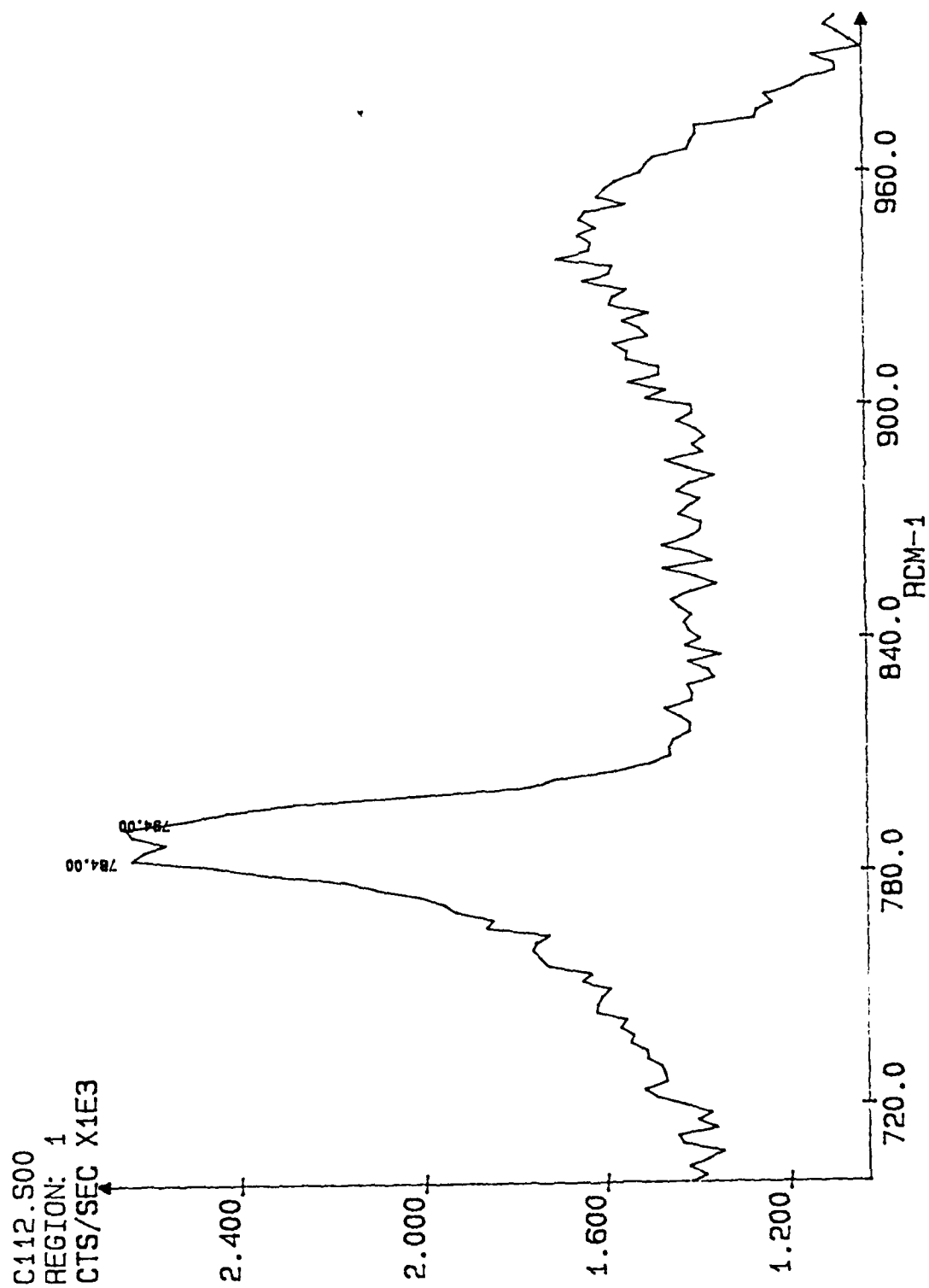
23

FIGURE 15 RAMAN SPECTRUM OF SAMPLE # 81. α-SiC peak is present at 784 cm^{-1} and β-SiC peak is present at 794 cm^{-1}.

to prevent achieving hermeticity. This silica tube was the second and final spare inner tube.

At this point in mid-May, the management of Diamond Materials, Inc. decided to stop work on this SBIR phase I program. The necessary parts required to resume experimentation would take ≈ two months to obtain. The contract had already exceeded its original six month duration. Also, DMI was committed to moving its entire laboratory and offices from State College, PA to Burlington, MA on May 25, 1990. Hence, despite over six months of effort, performance of the statement of work was limited to the CVD of β-SiC on silicon.

3.0 CONCLUSIONS

Because of chronic technical difficulties encountered with the heteroepitaxial growth of β-SiC on silicon substrates, the proposed method for synthesis of large area single crystal TiC (Section 1) has still not been tested. This program was DMI's first attempt at growing heteroepitaxial β-SiC on silicon substrates, although DMI had previously succeeded in heteroepitaxy of β-SiC on TiC crystals (grown by a float-zone method). The technical problems which limited progress included: (1) The mass flow controller for MTS frequently became clogged. The occlusion was probably due to MTS condensation or particulate formation in the capillary tube of the MFC. (2) Fracture of a critical ceramic part on the substrate susceptor assembly. An alumina collar was used to suspend the faceplate + sample + susceptor sandwich from above and was mounted at the end of a rod which rotated. The collar was attached to the susceptor by alumina bolts and nuts. However, the low thermal shock resistance of the machined alumina, coupled with its poor thermal expansion match to the graphite susceptor, led to the fracture of all three alumina collars which were made for this program. (3) The inner fused silica tubes tended to fatigue and fracture after repeated use. Again, all of the tubes obtained for this program eventually fractured.

Technically, the conclusions of this program are as follows:

(1)   The purpose of HCl/H_2 etch prior to CVD of β-SiC is to remove the outer several microns of silicon. This outer silicon contains a high concentration of crystallographic defects left behind by the chem-mechanical polishing procedure. The silicon at the bottom of the etch crater is rougher than original polished surface, but it is even and free of localized etch pits.

(2)   The HCl/H$_2$ etch and CVD of β-SiC can be performed at the same temperature, viz. 1300°C. A 5% HCl + 95% H$_2$ etch can be performed for 10 minutes immediately prior to introducing the SiC source gases. There is no need to cool the substrate to room temperature and heat up again between the HCl etch and deposition of SiC.

(3)   Growth of β-SiC on etched silicon at 1300°C can be achieved by using methyltrichlorosilane. The growth of a smooth, (possibly monocrystalline), β-SiC film may proceed in two stages. The initial microstructure is composed of discrete subgrains, each ≈ 1 - 3 μm in diameter, which are oriented cubically. As the film thickens, these subgrains may coalesce into a flat, uniform film. However, the subgrains beneath the SiC film create an "orange peel" texture in the top, smooth surface.

(4)   A reasonably pure, single phase β-SiC film was grown on off-axis silicon using 0.79% MTS diluted in H2 at 1300°C for 15 minutes.

4.0   RECOMMENDATIONS FOR FUTURE WORK

For the benefit of any organization wishing to continue the investigation of growth of large area TiC by CVD, DMI provides the following recommendations:

(1)   Re-design the inverted substrate assembly so that brittle, machined ceramic parts are not tightly bolted to a graphite susceptor heated to > 1300°C. The flaws left in the ceramic, coupled with thermal expansion mismatch of the ceramic to the graphite, eventually leads to fracture of the ceramic.

(2)   Use a mass flow controller for MTS specifically designed for controlling high vapor pressure liquids. These MFCs, recently marketed, do not require the liquid or vapor to pass through a capillary tube.

(3)   Perform etching of the silicon substrate as well as β-SiC deposition at the same temperature (1300°C) in rapid succession.

(4)   Use an alternative source gas for β-SiC. The corrosive nature of methyltrichlorosilane made it difficult to utilize. J. D. Parsons, formerly of Hughes Research, and Advanced Technology Materials have developed a proprietary source gas for β-SiC CVD which contains Si and C in a 1:1 stoichiometry. (J. D. Parsons, G. B. Kruval, and J. A. Vigil, in Amorphous and Crystalline Silicon Carbide II, ed. by Rahman, Yang and Harris, Springer-Verlag, New York, (1989) p. 171). This source gas

has been demonstrated to produce excellent ß-SiC films on TiC substrates; it should also deposit excellent heteroepitaxial ß-SiC films on Si substrates.